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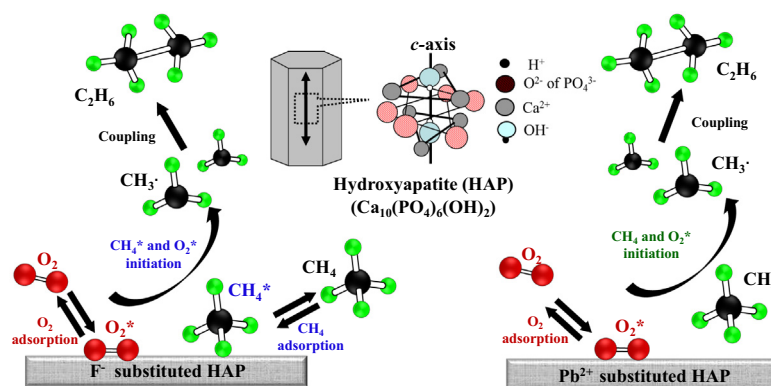
Catalytic consequences of cation and anion substitutions on rate and mechanism of oxidative coupling of methane over hydroxyapatite catalysts

Su Cheun Oh^a, Yu Lei^b, Huiyong Chen^c, Dongxia Liu^{a,*}^aDepartment of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States^bDepartment of Chemical and Materials Engineering, The University of Alabama in Huntsville, 301 Sparkman Drive, Huntsville, AL 35899, United States^cSchool of Chemical Engineering, Northwest University, Xi'an, Shaanxi 710069, China

HIGHLIGHTS

- Pb²⁺, F⁻ and both substitutions in hydroxyapatite (HAP) were studied.
- Both Pb²⁺ and F⁻ substitutions in HAP favored C₂H₆ formation.
- Kinetics of primary reactions on Pb-HAP and Pb-HAP-F was analyzed by Eley-Rideal mechanism.
- Kinetics of primary reactions on HAP and HAP-F was analyzed by Langmuir-Hinshelwood mechanism.
- Composition-catalytic performance correlations for HAP-based catalysts were established.

GRAPHICAL ABSTRACT



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ABSTRACT

The identity and rate constants of elementary steps in primary reactions of oxidative coupling of methane (OCM) over Pb²⁺ and/or F⁻ substituted hydroxyapatite (HAP, Pb-HAP, HAP-F, and Pb-HAP-F) catalysts have been studied. The rigorous kinetics analysis suggests that HAP and HAP-F initiated the reaction between adsorbed methane and O₂ following Langmuir-Hinshelwood behavior. The Pb-HAP and Pb-HAP-F, however, enabled the reaction between gaseous methane and adsorbed O₂ in the Eley-Rideal mechanism. The F⁻ substitution of OH⁻ weakened both O₂ adsorption and C–H bond activation, leading to low methane conversion and slightly higher C₂H₆ selectivity. The substitution of Ca²⁺ by Pb²⁺ weakened both methane and oxygen adsorptions, but maintained C–H bond activation and raised C₂H₆ selectivity. The present analysis explored for the first time the effects of cation and/or anion in HAP on OCM reactions in which the analysis has been detailed and quantified in the nature of the mechanism-based kinetic models.

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1. Introduction

The oxidative coupling of methane (OCM) involves the reaction of methane (CH₄) and oxygen (O₂) over a catalyst at high temperatures to form C₂ (C₂H₆ and C₂H₄) hydrocarbons. The nature of

* Corresponding author.

E-mail address: liud@umd.edu (D. Liu).

one-step reaction to C₂ products in OCM reactions is of great significance and has been a continuous interest in the past few decades [1–4]. A variety of catalysts, including alkali [5–7], alkaline earth [8–12], rare earth [13–15] and transition metal oxides [16–18], have been broadly studied in OCM reactions. The general accepted mechanism of OCM reactions [19–21] is a mixed homogeneous-heterogeneous reaction network, in which methyl radicals (CH₃) are formed on the catalyst surface by methane activation, desorbed as free CH₃ radicals, and then recombined to form ethane (C₂H₆) as a primary product and ethylene (C₂H₄) as a secondary product from the subsequent dehydrogenation of C₂H₆. Simultaneously, methyl radicals undergo deep oxidation by adsorbed diatomic oxygen species and gas phase molecular oxygen (O₂), respectively, to produce CO₂ and CO.

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) is a type of calcium phosphate crystal, more commonly studied in biomaterials since it is the major component in bone and teeth [22,23]. The Ca²⁺ cation and the anion, either PO₄³⁻ or OH⁻, in HAP can be substituted by other cations and/or anions to endow HAP with tunable thermal and chemical stability, catalytic properties, and ion/electronic conductivity [24–28]. Lead cation (Pb²⁺) substituted HAP (Pb-HAP) has been studied as a catalyst for OCM reactions. It is shown that Pb-HAP was able to increase C₂ selectivity by a factor of ~5 compared to bare HAP [29–31]. The enhancement in OCM performance of Pb-HAP was ascribed to the stabilization of methyl radicals by Pb²⁺ sites for pairwise reactions against oxidation reactions [32]. The anion substitution such as halide-substituted HAP has been reported to enhance the acid resistance and mechanical properties of HAP bioceramics [33] and to reduce the number of oxygen species that are resulted from –OH groups in oxidative dehydrogenation of alkanes [34]. The substitution of HAP with both cation Pb²⁺ and fluoride anion (F⁻) has not been explored in literature, but has potential to concurrently improve the thermal/chemical stability and catalytic activity of HAP in OCM reactions.

Selectivities and yields of C₂ products in OCM reactions depend on the identity and dynamics of specific elementary steps involved in the primary and secondary reaction steps on the catalysts. Even though the performance of Pb-HAP in OCM reactions has been studied and the enhancement in C₂ selectivity upon Pb²⁺ substitution in HAP has been justified [29,35], no rigorous kinetic study is available on the kinetics and mechanisms of OCM reactions on this catalyst. In addition, the effects of both cation and anion substituted HAP catalyst on the elementary steps of OCM reaction is yet to be determined. A detailed understanding of the kinetic networks is essential to describe the reaction steps in terms of their rate constants and to define the specific contributions of cation and anion compositions in HAP-based catalysts. On the basis of this understanding, a catalyst composition with desired catalytic performances can be developed for OCM reactions.

Herein, we report the synthesis and characterization of HAP catalysts with Pb²⁺ cation (Pb-HAP), F⁻ anion (HAP-F), and both cation and anion (Pb-HAP-F) substitutions. The influences of cation and/or anion substitutions in HAP on the rate and selectivity of OCM reactions together with identity and reaction rate constants of elementary steps in primary reactions of OCM were also examined. The results show that HAP and HAP-F followed Langmuir-Hinshelwood reaction pathway in which the reaction occurred between associatively adsorbed O₂ and CH₄ species. The Pb-HAP and Pb-HAP-F catalysts, however, followed Eley-Rideal reaction pathway in which the reaction occurred between gaseous CH₄ and associatively adsorbed O₂ species. The substitution of Ca²⁺ by Pb²⁺ in HAP preserved C–H activation in CH₄ and improved C₂ selectivity due to the stabilization of methyl radicals by Pb²⁺ sites for pairwise reaction despite impaired CH₄ and O₂ adsorption capabilities. The substitution of –OH groups by F⁻ in HAP weakened both O₂ adsorption and C–H bond activation compared to HAP,

leading to low methane conversion and diminished CO₂ formation but higher C₂ selectivity. The Pb-HAP-F exhibited highest C₂ selectivity in the tested four HAP-based catalysts, which can be attributed to the integration of methyl radical pairwise reaction and reduced oxygen species on the catalyst in OCM reactions. The present study rigorously explored the mechanisms of OCM reactions and influences of cation and/or anion substitutions in HAP structure on the primary steps of these reactions.

2. Experimental

2.1. Materials

Ammonium phosphate dibasic ((NH₄)₂HPO₄, ≥99.0%), ammonium chloride (NH₄Cl, ≥99.5%), ammonium fluoride (NH₄F, A.C.S. Reagent, ≥98.0%) and ammonia hydroxide solution (NH₄OH, 28–30%) were supplied from Sigma-Aldrich. Lead nitrate (Pb(NO₃)₂, ACS. Reagent) was purchased from J.T. Baker while calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, 99.0–103.0%) was purchased from Alfa-Aesar.

2.2. HAP-based catalysts preparation

The synthesis of HAP-based catalysts was carried out by a coprecipitation method, as described in our previous work [36]. In the synthesis of bare HAP, 0.24 M of (NH₄)₂HPO₄ solution and 0.40 M of Ca(NO₃)₂ solution were prepared in two flasks separately. NH₄OH was added to each source solution to adjust the pH to ~10. Ca(NO₃)₂ solution was preheated to 363 K in an oil bath equipped with reflux condenser. After that, (NH₄)₂HPO₄ solution was added to the preheated Ca(NO₃)₂ solution dropwise via a syringe pump in 2 h. After addition of the (NH₄)₂HPO₄ solution, a cloudy reaction suspension was obtained and the suspension was kept at 363 K under magnetic stirring for 24 h followed by aging for 24 h at room temperature. Lastly, the product was collected by centrifugation at 6000 rpm for 5 min and washed with deionized (DI) water to remove any undesirable ions. The centrifugation and washing steps were repeated 5 times. The resulted wet product was dried in a vacuum oven at 343 K overnight.

As for the synthesis of HAP-F catalyst, the same procedure as that for bare HAP was applied except that a solution consisting of 0.16 M of (NH₄)₂HPO₄ and 0.08 M of NH₄F was prepared to replace 0.24 M of (NH₄)₂HPO₄ solution. In the synthesis of Pb-HAP-F catalyst, the Ca(NO₃)₂ solution used in bare HAP synthesis was replaced with a solution consisting of 0.32 M of Ca(NO₃)₂ and 0.08 M of Pb(NO₃)₂. The remaining procedures were the same as that for HAP-F catalyst. Pb-HAP was prepared using procedures reported previously [31], which was similar to the synthesis of bare HAP above except that an aqueous solution of Pb(NO₃)₂ (0.08 M), Ca(NO₃)₂ (0.32 M) and NH₄Cl (1.3 M) was prepared to replace 0.40 M of Ca(NO₃)₂ in HAP synthesis.

All the dried HAP-based catalysts were treated in flowing air (150 mL min⁻¹, ultrapure, Airgas) at 973 K for 5 h at a ramp rate of 17.5 K min⁻¹ from room temperature. The catalyst samples were subsequently pelleted, crushed and sieved to retain particle sizes between 180 and 425 μm (40–80 mesh) for characterization and catalysis experiments discussed below.

2.3. Catalyst characterization

Scanning electron microscopy (SEM) images were taken on a Hitachi SU-70 electron microscope to visualize the morphologies of the HAP-based catalysts. N₂ adsorption-desorption isotherms of the samples were measured using an Autosorb-iQ analyzer (Quantachrome Instruments) at 77 K. The samples were outgassed

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